PREPARATION OF ELECTRODE COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to processes for the preparation of electrode compositions, especially those intended for use in supercapacitors, and to methods of forming electrodes and cells containing or derived from those compositions. The invention also relates to an improved method for synthesising lithium sulphite.

BACKGROUND OF THE INVENTION

Batteries can store lots of energy but have low power, taking a long time to charge or discharge. Conventional capacitors have enormous power but can usually only store tiny amounts of energy. Supercapacitors offer a unique combination of high power and high energy. When a supercapacitor is charged, there is no chemical reaction, rather energy is stored as a charge or concentration of electrons on the surface of a material. Supercapacitors can therefore charge and discharge at high rates since only charge transfer is involved, and can undergo a large number of cycles without any apparent degradation (e.g. >100,000 cycles).

Supercapacitors, also known as ultracapacitors, or electrochemical double layer capacitors (EDLC) use a double layer of high surface area carbon separated by an exceedingly thin insulator to achieve high capacitance. In a paper entitled "Novel Supercapacitors", p 68, Proceedings of the 40th Power Sources Conference, Cherry Hill, USA, Jun. 10-13, 2002 (hereinafter referred to as the "2002 paper"), one of the present inventors, inter alia, disclosed a new type of supercapacitor where, in addition to the double layer capacitance, additional capacitance or "pseudo-capacitance" was obtained using nitrogen-containing carbon polymers where complexes had been incorporated at certain nitrogen sites, migration of solution species towards and away from these sites giving rise to this pseudo-capacitance.

In the 2002 paper, polyacrylonirile (PAN) was used as a cheap and readily available polymer. Pyrolysis of PAN leads to increasingly complex, conjugated and cyclised molecules containing nitrogen in pyridine-like rings, but it was found that N content decreases with increased heating, as illustrated in FIG. **3** below. Steps were therefore taken to obtain a pyrolysed PAN with a sufficient N content but also with a suitably high surface area, open, porous structure that would permit complex formation and ion species migration. The pyrolysed PAN was then combined with lithium sulphite, Li_2SO_3, with the aim of subsequently forming N:sulphur trioxide SO_3 complexes at the nitrogen sites. The 2002 paper describes lithium sulphite as being incorporated in the pyrolysed polymer and then provided as an electrode in a cell where, upon charging, the lithium sulphite was electrolysed to form sulphur trioxide, which subsequently complexed with nitrogen in the pyrolysed PAN. Supercapacitor cells made from those modified electrodes were found to have increased capacitance as compared with unmodified PAN electrodes (i.e. without complexed N sites).

One of the authors of the 2002 paper also filed two patent applications published as GB2266179 and GB2335073, respectively. GB2266179 teaches secondary cells in which the cathode (positive electrode) composition consists of a solid complex of sulphur trioxide and a polymeric tertiary amine (the complex being formed by a previous chemical reaction) and the anode is lithium. GB2335073 describes GB2266179 as disclosing electrochemical cells with low energy densities due to the high ratios of carbon to nitrogen functionality. GB2335073 itself is directed to improved secondary cells with similar light metal anodes and similar cathodes of N—C polymers complexed with sulphur trioxide except that these polymers have conjugated imine functionality, preferably formed by thermally restructuring nitrile containing polymers. GB2335073 teaches that charging of the secondary cells causes lithium to be electroplated at the anode and discharging causes recombination of lithium with the SO_3 complexes: hence, it states that SO_3 acts not only as polymer dopant but also as sites for the reversible redox electrochemistry of Li_2SO_3.

Journal of the Chemical Society, pages 2245-8, (1928), describes a method for synthesising lithium sulphite in which a mixture of hydrogen and sulphur dioxide is passed through lithium carbonate solution until effervescence ceases, and the flask is then heated while passing through dry hydrogen (to prevent oxidation) until anhydrous lithium sulphite is produced. Since sulphur dioxide is a corrosive gas, and hydrogen is a flammable gas, this process is not ideal.

SUMMARY OF THE INVENTION

The present invention is directed towards providing improved methods for forming SO_3 complexed electrode materials, including providing an improved method of synthesising Li_2SO_3.

The present invention provides, in a first aspect, a process for preparing lithium sulphite comprising the following steps:

a) introducing H_2SO_3 (aq) into a reaction vessel;

b) reacting the H_2SO_3 (aq) with an aqueous suspension of Li_2CO_3 in the vessel to form an aqueous solution of Li_2SO_3; and,

c) evaporating the solution to recover Li_2SO_3(s), wherein at least steps a) and b) are conducted under an inert atmosphere.

By introducing the SO_3 functionality into the reactor in the form of sulphurous acid, the use of hazardous gases is avoided and the amount and rate of acid addition can be carefully controlled. The process is usually conducted as a batch process in a reaction vessel maintained under an inert atmosphere (e.g. N_2 or Ar), and usually at a raised pressure to prevent air influx. No other reactants or catalysts will usually be present.

Ideally the two reactants are reacted in substantially equimolar amounts (that is up to +−3%) and this may be achieved by adding H_2SO_3 (aq) by titration. An excess of lithium carbonate in the final product would contaminate the electrode material, while an excess of acid would lead to the undesirable formation of $LiHSO_3$. Li_2CO_3 is only sparingly soluble in water whereas Li_2SO_3 is very soluble, and hence, the end point of the reaction is clearly identified by the point where the solution (previously a white emulsion) goes clear and colourless, and effervescence ceases; at this point the pH is usually ~pH 7-7.5.

It is crucial that the actual reaction is carried out under an inert atmosphere as Li_2SO_3 is readily oxidised to Li_2SO_4 in the presence of water. The lithium carbonate solution should usually be pre-flushed with inert gas. The H_2SO_3 should also preferably be pre-flushed with inert gas and held in a sealed vessel, being added in incremental amounts to avoid SO_2 fuming. Also the inert gas purging is preferably conducted from the bottom of the reaction vessel, while titration occurs from above, to minimise loss of SO_2 from the H_2SO_3. In step c) care should still be taken to minimise oxidation and hence the evaporation should preferably be conducted under vacuum, or inert gas purging should preferably continue.